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Log  $\chi^2$  Distribution of Correlation Times Revisited

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### ABSTRACT

The log- $\chi^2$  distribution of correlation times and its application to polymer systems are examined. It is found that the original mean correlation-time parameter,  $\tau_0$ , (*Macromolecules*, 1973, 6, 882) does not represent the true mean of the distribution. A properly parameterized log- $\chi^2$  distribution and function relating the original  $\tau_0$  and width parameters,  $p$  and  $b$ , to the true mean are derived. Fitting of both the original log- $\chi^2$ , corrected log- $\chi^2$ , and log-normal distribution to experimental data is discussed and the log-normal distribution being proposed as an alternative. Interpretations of NMR data from polymer/solvent systems can be different for the log- $\chi^2$  and log-normal distributions. Due to its better defined moments, the log-normal's results are believed to be more physically realistic when large widths are required.

Often, definitive models for molecular motion do not exist or fail to give reasonable results. And, as an approximation, an exponential decay of correlation with a distribution of correlation times is used as the correlation function. Such distributions prove very useful, especially for polymers and polymer solutions, at describing and quantifying the dynamics.<sup>1-8</sup>

Heatley<sup>8</sup> has summarized the successes and failures of several of the distributions used to describe polymer dynamics. Of these, the asymmetric log- $\chi^2$  distribution has had good success in fitting data from a broad range of techniques including NMR, ESR, and dielectric studies.<sup>1,2,5,8</sup> We have found that the use of the log- $\chi^2$  distribution may occasionally yield parameters which should not be compared from system to system. In some cases, a proper comparison can be made with the application of a correction factor. For example, the application of the log- $\chi^2$  distribution, as proposed in the literature,<sup>1</sup> to NMR relaxation data of toluene in polystyrene generated a slower mean rotational correlation time for pure toluene than it did for motionally hindered toluene near polystyrene at the same temperature. It also yielded unphysical results in a dynamics study of poly(*iso*-propyl acrylate) (PIPA).<sup>7</sup> In that study, the mean correlation time predicted by the log- $\chi^2$  distribution had little correlation with polymer concentration, often being faster for more concentrated solutions than for less concentrated ones at the same temperature. Other models employed to quantify the PIPA system suffered similar problems. After examining the log- $\chi^2$  distribution, we found that the parameter  $\tau_0$ , previously interpreted as the mean correlation time, is not the true mean, but rather a scaling factor which can be related to the true mean.

A normalized, scaled, base  $b$  log- $\chi^2$  distribution,  $F^\chi(\tau_c; b, p, \theta)$ , has the form of:

$$F^\chi(\tau_c; b, p, \theta) = \frac{1}{\theta} \frac{\left(\frac{p}{\ln(b)}\right)^p}{\Gamma(p)} \left(\ln\left(\frac{\tau_c}{\theta} + 1\right)\right)^{p-1} \left(\frac{\tau_c}{\theta} + 1\right)^{-(p/\ln(b)+1)} \quad \text{for } 0 \leq \tau_c \leq \infty \quad (1)$$

with  $\tau_c$ ,  $b$ ,  $p$ ,  $\theta$ , and  $\Gamma$  the correlation time, numerical base, width parameter, scaling parameter, and gamma function, respectively. The superscript  $\chi$  denotes the log- $\chi^2$  distribution. The

parameter  $b$  is often fixed at 1000, but it could be replaced with  $e$ , the natural base. The mean,  $\tau_0^\chi(b, p, \theta)$ , of  $F^\chi(\tau_c; b, p, \theta)$  is:

$$\tau_0^\chi(b, p, \theta) = \int_0^\infty \tau_c F^\chi(\tau_c; b, p, \theta) d\tau_c = \theta \left[ \left( \frac{p}{p - \ln(b)} \right)^p - 1 \right] \quad (2)$$

Experiments often probe the dynamics through the Fourier transform of the correlation function or spectral density,  $J(\omega)$ . For a distribution,  $F(\tau_c)$ , of exponentially decaying correlation times,  $J(\omega)$  is:

$$J(\omega) = \int_0^\infty \frac{2 F(\tau_c) \tau_c}{1 + \omega^2 \tau_c^2} d\tau_c \quad (3)$$

where  $\omega$  and  $\tau_c$  are the frequency and correlation time, respectively.  $F^\chi(\tau_c; b, p, \theta)$  could be used in equation (3) and the mean correlation time calculated from equation (2) after determining the parameters  $b$ ,  $p$ , and  $\theta$ . However, transforming the distribution and spectral density to a reduced correlation time will allow a more direct comparison with the original work<sup>1</sup> and eliminate the need for equation (2) as the scaling parameter,  $\theta$ , will be replaced by a mean correlation-time parameter,  $\tau_0$ .

With the transformation  $\tau_r = \tau_c / \tau_0^\chi(b, p, \theta)$  applied to  $F^\chi(\tau_c; b, p, \theta)$ , the log- $\chi^2$  distribution of reduced correlation times,  $G^\chi(\tau_r; b, p)$ , is:

$$G^\chi(\tau_r; b, p) = \frac{\left( \frac{p}{\ln(b)} \right)^p}{\Gamma(p)} \tau_0^\chi(b, p, 1) \left( \ln(\tau_r \tau_0^\chi(b, p, 1) + 1) \right)^{p-1} \left( \tau_r \tau_0^\chi(b, p, 1) + 1 \right)^{-(p/\ln(b) + 1)} \quad (4)$$

For simplicity,  $\theta$  is set to one in the argument as the transformation eliminates any  $\theta$  dependence. Similarly,  $J(\omega)$  becomes:

$$J(\omega) = \int_0^{\infty} \frac{2 G\chi(\tau_r; b, p) \tau_r \tau_0}{1 + \omega^2 \tau_r^2 \tau_0^2} d\tau_r \quad (5)$$

where  $\tau_0$  has replaced  $\tau_0^\chi(b, p, \theta)$  and, consequently, represents the true mean of the distribution.

If  $F\chi(\tau_c; b, p, \theta)$  had been scaled by the *parameter*  $\tau_0$ , as in reference (1), instead of  $\tau_0^\chi(b, p, \theta)$ ,  $\tau_0$  of equation (5) would not be the true mean, but a scaling parameter. The mean correlation time could then be calculated from:

$$\langle \tau_c \rangle = \int_0^{\infty} \tau_c F\chi(\tau_c; b, p, \theta) d\tau_c = \tau_0 \int_0^{\infty} \tau_r G\chi(\tau_r; \tau_0, b, p, \theta) d\tau_r \quad (6)$$

where  $G\chi(\tau_r; \tau_0, b, p, \theta)$  is  $F\chi(\tau_c; b, p, \theta)$  scaled about the *parameter*  $\tau_0$ . Being scaled about  $\tau_0^\chi(b, p, \theta)$  simplifies matters by cancelling any previous scaling and making the mean of  $G\chi(\tau_r; b, p) = 1$  and, so,  $\langle \tau_c \rangle = \tau_0$ .

For comparison, the spectral density (equation (5)) can be put into a form similar to equation (25) of reference (1):

$$J(\omega; \tau_0, b, p) = \int_0^{\infty} \frac{2 \chi^2(s, p) [e^s - 1] \tau_0}{\left[ \left( \frac{p}{p - \ln(b)} \right)^p - 1 \right] \left[ 1 + \omega^2 \tau_0^2 \left( \frac{[e^s - 1]}{\left( \frac{p}{p - \ln(b)} \right)^p - 1} \right)^2 \right]} ds \quad (7)$$

where  $p$ ,  $b$ , and  $\omega$  are as defined previously,  $s$  is an integration variable,

$$\chi^2(s, p) = \frac{p^p}{\Gamma(p)} s^{p-1} e^{-s} \quad (8)$$

and  $\tau_0$  is the mean correlation time of the distribution.

The relationship between the true mean,  $\tau_0$ , of equations (5) and (7) and the originally reported mean,<sup>1</sup>  $\tau_0^{\text{org}}$ , can be calculated from equation (6) and is:

$$\tau_0 = \tau_0^{\text{org}} \frac{\left( \frac{p^{\text{org}}}{p^{\text{org}} - \ln(b^{\text{org}})} \right)^{p^{\text{org}}} - 1}{b^{\text{org}} - 1} \quad (9)$$

where the superscript *org* indicates parameters that were fitted from the original distribution. Depending on  $b$  and  $p$ , *this could be a large correction* and, consequently, responsible for the  $\text{log-}\chi^2$ 's previously reported unphysical behavior. Also, this equation and the distribution itself are only valid for  $p > \ln(b)$  where the distribution is normalizable. The possible limitations of the distribution and its dependencies on  $p$  and  $b$  are clarified by examining the moments of  $G\chi(\tau_r; b, p)$  which are:

$$\langle \tau_r^n \rangle = \int_0^\infty \tau_r^n G\chi(\tau_r; b, p) d\tau_r = \sum_{i=0}^n \binom{n}{i} (-1)^{n-i} \left( \frac{p}{p-i \ln(b)} \right)^p \left( \left( \frac{p}{p-\ln(b)} \right)^p - 1 \right)^{-n} \quad (10)$$

where  $\binom{n}{i}$  is the binomial coefficient. The original distribution has a similar form for its moments. For large values of  $p$ , the moments are essentially independent of  $b$ . For the intermediate values,  $\ln(b)$  scales  $p$  to smaller values, making the distribution wider for a given  $p/\ln(b)$  ratio. Finally, for small values of  $p$ , the dependence is unclear as the moments are infinite. This behavior suggests that the natural base  $e$  should work as well as any other, i.e. 1000, as long as  $p$  is not restricted to integer values. Indeed, with non-integer  $p$  values, all data tested fit equally well and with the same predicted  $\tau_0$  using either  $e$  or 1000 as the base.

To test the corrected  $\text{log-}\chi^2$  distribution's ability to fit polymer data and yield physically meaningful results, we used it to fit four data sets: polystyrene, polyisoprene, and polybutadiene  $^{13}\text{C}$   $T_1$ - $T_2$  (20.6 MHz) data from the original paper<sup>1</sup>; polyisoprene  $^{13}\text{C}$   $T_1$  (20.1 and 100.6 MHz) data<sup>5</sup>; poly(*iso*-propyl acrylate)- $d$  in chloroform  $^2\text{H}$   $T_1$ - $T_2$  (13.8 MHz)<sup>7</sup> data; and, toluene- $d_5$  in polystyrene  $^2\text{H}$   $T_1$ - $T_2$  (30.7 MHz) data.<sup>6</sup> These systems represent a wide variety of polymer dynamics, namely bulk polymer dynamics, solution state polymer dynamics, and solvent dynamics in polymer solutions.

For the polymer data in the original paper, the mean correlation times,  $\tau_0$ 's, from both the original and modified log- $\chi^2$  seem physically reasonable for polystyrene in o-dichlorobenzene and bulk polyisobutene. However, the original distribution yielded an unusually fast  $\tau_0$  of 0.1 ns for bulk polybutadiene. Using equation (9), this  $\tau_0$  became 5 ns, the same value fit from the modified distribution. This seems more reasonable. In general, the modified log- $\chi^2$  distribution generates larger  $\tau_0$ 's than the original. But, with the use of equation (9) *both distributions* yield the same  $\tau_0$ , with smaller values of  $p$  requiring larger corrections. These results are typical of *all* the data fit in this paper.

Unlike  $T_1$ - $T_2$  data investigated, both the modified and original (in conjunction with equation (9)) log- $\chi^2$  distributions generate unrealistically long  $\tau_0$ 's from the polyisoprene  $^{13}\text{C}$   $T_1$  data.<sup>5</sup> Table I lists the results from the  $^{13}\text{C}$  data. The reason the log- $\chi^2$  distribution fails for the  $^{13}\text{C}$  data is not clear. It may be linked to its undefined moments and that the  $^{13}\text{C}$  data only samples the distribution in the MHz region. As can be seen from Table I, the modified log- $\chi^2$  compares well until  $p$  becomes less than  $2 \cdot \ln(b)$  below which only the log- $\chi^2$ 's first moment exists. For these values of  $p$ , the distribution's tail is poorly parameterized and large correlation times may be unduly weighted. To successfully fit data to such a distribution, some constraints on the tail, as the zero frequency  $T_2$  data imposes, would probably help give more reasonable results.

As an alternative to low frequency data, the log-normal distribution might be used. Its moments exist; so, its tail and skew are well defined.<sup>9</sup> In general, it has simple dependencies on its parameters (easy to fit); is well behaved with well defined moments; and, is more skewed than the log- $\chi^2$ . It also affords a simple physical interpretation of the underlying processes.<sup>10,11,12</sup> The distribution of reduced correlation times,  $G(\tau_r; \sigma)$ , for the log-normal distribution is:

$$G(\tau_r; \sigma) = \frac{1}{\sqrt{\pi} \sigma \tau_r} e^{-(\ln(\tau_r)/\sigma + \sigma/4)^2} \quad (11)$$

which would replace  $G\chi(\tau_r; b, p)$  in equation (5). Its second moment is:

$$\langle \tau_r^2 \rangle = e^{\sigma^2/2} \quad (12)$$



and its mean is one, as expected from the scaling.

The log-normal distribution fit *both* the  $T_1$ - $T_2$  and  $^{13}\text{C}$   $T_1$  data discussed earlier with vanishing error and few iterations of the fitting algorithm.<sup>13</sup> For these data, except for where log- $\chi^2$  failed, the  $\tau_0$ 's were essentially identical between the modified log- $\chi^2$  and the log-normal, differing from the original log- $\chi^2$  according to equation (9). As mentioned previously, the predicted magnitudes and trends of the  $\tau_0$ 's were more realistic than those of the original log- $\chi^2$  and, for the PIPA data, also more realistic than other models employed<sup>7</sup> (compare Figure 1 to similar plots in reference (7)). That is, the  $\tau_0$ 's increased with increasing polymer concentration or decreasing temperature, realistic in an intuitive sense.

For reference (5), the main difference between the log-normal and the original log- $\chi^2$  is that the log-normal predicts a *higher* apparent activation energy for the high temperature data and a *10 fold increase* in  $\tau_0$  at low temperatures. As in the reference (5), the NOEF's were not used in the fitting procedure. They offer an independent test of each distribution's predictive ability. Unfortunately, the calculated NOEF's follow the experimental values for all the distributions and no distinction can be made. For extremely broad distributions, however, the log-normal has a limiting,  $\tau_0$  independent, NOEF value of 1.33 compared to the log- $\chi^2$ 's value of 0.9 (at 20 Mhz). This increase is presumably due to the larger skew of the log-normal distribution. None of the experimental data required broad enough distributions to test this difference.

In conclusion,  $\tau_0$  of the original log- $\chi^2$  distribution is a scaling parameter which is often, but not always, representative of the mean. Comparisons and predicted trends may be on different scales unless a correction to the true mean (equations (6) and (9)) is made. Modifying the distribution yields a new distribution in which  $\tau_0$  is the true mean. However, both the original and modified log- $\chi^2$  distribution have limited use as their moments can be ill-defined and careful sampling of the frequency space is required. We prefer the log-normal distribution as it is better skewed, and has well defined moments and simple derivatives. Its ability to fit and give physically

reasonable results from low and high frequency  $T_1$ - $T_2$  data as well as solely high frequency  $T_1$  data indicates that it may be useful where the log- $\chi^2$  appears unphysical.<sup>6,7,8,14,15</sup>

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$$\%error = \sum_{i=1}^2 \left( \frac{T_i^{exp} - T_i^{calc}}{T_i^{exp}} \right)^2$$

were  $10^{-6}$  for both Schaefer's original distribution and the modified log- $\chi^2$  and  $10^{-30}$  for the log-normal. For all log- $\chi^2$ 's, the number of iterations ranged from 20 to 2000, depending on the quality of the initial guesses. For the log-normal, the number of iterations was always less than 50, independent of the initial guess.

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Table I

Fits to the  $\text{C}_1$  methylene  $^{13}\text{C}$   $T_1$  data of reference (5) ( $M_n = 7$  kg/mol) ( $b = 1000$ )

T (K)	$T_1(100\text{MHz})$ (s)	$T_1(20\text{MHz})$ (s)	$\text{log-}\chi^2_{\text{org}}^{\text{a}}$		$\text{log-}\chi^2_{\text{org}}^{\text{b}}$		$\text{log-}\chi^2_{\text{mod}}^{\text{c}}$		$\text{log-normal}^{\text{d}}$	
			$\tau_0$ (ns)	p	$\tau_0$ (ns)	p	$\tau_0$ (ns)	p	$\tau_0$ (ns)	$\sigma$
293	0.152	0.035	2.00	7	1.90	7.3	$340 \cdot 10^3$	7.5	20.0	3.45
303	0.156	0.043	1.00	7	0.67	8.0	5500	8.0	7.10	3.36
313	0.168	0.053	0.40	8	0.31	9.4	71.2	9.5	3.30	3.27
323	0.185	0.068	0.17	11	0.17	11.5	6.48	11.5	1.40	3.07
333	0.210	0.090	0.10	14	0.10	14.0	1.41	14.0	0.660	2.86
343	0.239	0.135	0.073	24	0.076	23.3	0.272	23.5	0.240	2.25
353	0.275	0.192	0.062	34	0.064	35.7	0.139	35.7	0.130	1.80
363	0.323	0.255	0.053	45	0.054	45.6	0.097	45.6	0.095	1.57
373	0.378	0.310	0.043	47	0.044	45.7	0.079	45.7	0.078	1.58
$E_a$ -High Temp. (kJ)			18.6		19.6		43.6		38.7	
$E_a$ -Low Temp. (kJ)			63.0		59.2		257 <sup>e</sup>		68.5	

<sup>a</sup> fit by Denault and Prud'homme using original  $\text{log-}\chi^2$ ;<sup>b</sup> recalculated data using original  $\text{log-}\chi^2$  and non-integer  $p$ 's;<sup>c</sup> modified  $\text{log-}\chi^2$ , equation (4);<sup>d</sup> log-normal distribution, equation (11);<sup>e</sup> see text for explanation.

**Figure Caption**

**Figure 1.**  $\tau_0$  values from the log-normal distribution's fit to  $^2\text{H}$   $T_1$  and  $T_2$  data (reference (7)) as a function of temperature and PIPA concentration. The curves drawn are for visual clarification.

